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Biodegradable Polymers – A Tutorial for a Circular Plastics Economy

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1.1 Context

From the appearance of the first bakelite object in the early twentieth century to the ban on certain single-use plastics in 2021 in the EU, the modern world has changed drastically due to the advent of synthetic plastics. Although the mass production of most plastics – notably polypropylene and polyethylene – only truly started in the 1950s, the cumulative volumes produced since have grown rapidly [1–3]. This growth comes from their utility on our comfort, convenience, and health that plastics have delivered so far and, arguably, will deliver in the future – the age of 3D printing at home has just begun. However, these benefits also come at a price. There is a growing accumulation of plastic litter on land, in rivers and seas all over the world, and even inside living organisms along the whole food chain, from mussels to birds and mammals. Best exemplifying the scale of the issue are the plastic soups, i.e. concentrated floating plastic debris in all major subtropical ocean gyres. Sources estimate that more than 67% of the plastic marine load originates from 20 major rivers [3].

This pollution problem has two main root causes. The first and most important one is us, the consumers, that are discarding waste plastic without consideration for the consequences and/or, by lack of proper waste collection infrastructure. Corporations also cause spillage and ill-disposal. Plastics were never meant to end up in the environment, although little consideration has been given to their end-of-life in the first 50 years since their mass production. As a matter of fact, nowadays 30% of the production is littered, notwithstanding an additional 40% that ends up in landfill and waste dumps [1]. The second root cause is the high chemical stability of the materials: plastics should indeed be considered as persistent pollutants that were never present together with fauna and flora during their almost four billion years of evolution.
The first root cause would be subject of a book on social and political science and will be kept out of scope here. But the second is a consequence of technology, leaning close to the purpose of this book. Is there a reason to run the plastics economy further with almost completely inert materials, or do we have alternatives that lead us to a new plastics economy, as advocated by the Ellen McArthur Foundation? [1]. Of course, as the challenges of the current plastics industry are rapidly urging us to take actions, we foresee interwoven debate and regulations to align both root causes.

Diving to the heart of technological issue, the book aims at presenting a comprehensive view on biodegradable plastics, encompassing a range of aspects from synthesis, e.g. based on renewable resources, to properties and applications, recycling, biodegradation, and environmental impacts as well as business challenges. The following sections will summarize and analyze for you the 13 chapters of the book with a critical look, extract their major learnings, and formulate an outlook for the future of biodegradable plastics. The structure of the book is visually outlined in Figure 1.1.

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Figure 1.1 Visual outline of the book with its 14 chapters [4–16] divided thematically. Source: Lilly Jenisch is thanked for making this figure.
1.1 Context

But the plastic litter is not the sole problem to solve to develop a truly circular economy. The chemical industry also needs to disconnect from fossil hydrocarbons as feedstock and energy sources and minimize all its emissions, particularly eliminating those greenhouse gas emissions that contribute to climate change [2]. Accordingly, the industry must eventually switch to recycled and renewable carbon as feedstock for chemicals and plastics [2]. A major role is therefore laid down for the use of atmospheric CO₂, via sustainable biomass or direct air capture, to produce sustainable plastics. These sustainable plastics represent the nexus of plastic litter and climate change. They will therefore be an inevitable subject of discussion in this book on biodegradable plastics.

The book kicks off by sketching the generation of plastic litter and its environmental impact (Chapter 3, [4]) and analyzing the mechanisms of biodegradation (Chapter 2, [5]) as potential remediation to the problem (Chapter 3). Before diving into the different types of (semi-)degradable plastics out there, the book reviews today’s polymers, both fossil- and bio-based (Chapter 4, [6]), their manufacture, properties, and applications. Among the various families of potentially biodegradable polymers, polyesters (Chapters 5–7, [7–9]) and polysaccharide-based plastics (Chapters 8 and 9 [10, 11]) feature prominently, but lignin-derived materials (Chapter 10, [12]) and more specialized recyclable thermosets – vitrimers – (Chapter 11, [13]) are also covered. Going beyond these technical options, degradable plastics are discussed in relation to plastic waste (end-of-life) management (Chapter 12, [14]) and from a life-cycle (analytical) perspective (Chapter 13, [15]). Finally, business challenges and marketing strategies for launching new polymers are outlined (Chapter 14, [16]).

Before diving into the heart of the subject, we wish to clarify a few points of confusion: the difference between biodegradable, compostable, bio-based, and bioplastics. These labels are often assumed to cover the same plastics and to oppose them to the traditional fossil-based plastics. But bio-based origin and biodegradable function are in fact unrelated; the former refers to its source while the latter to its end-of-life [17]. Bio-based plastics are literally derived from biological feedstocks, being from animal, vegetal, or other living organisms (e.g. fungi and bacteria). Many of them show significant biodegradability, but others are equally environmentally persistent as today’s fossil plastics. For instance, biological feedstocks are sometimes the source for molecular structures that are identical to or resemble those derived from fossil feedstock and, therefore, show a similar lack of biodegradability. An obvious example is the inert bio-based polyethylene that is produced by converting sugars to ethanol, ethylene, and finally polyethylene. Along the same line, however, a limited number of fossil-based plastics show chemical structures that are readily biodegradable, as illustrated by oil-based polycaprolactone (PCL) (Chapter 7). We also need to differentiate compostable from biodegradable plastics. Compostable plastics are a sub-family of biodegradable plastics; they degrade most swiftly to make industrial composting affordable, as discussed below. Finally, we would recommend to avoid using the label “bioplastics” that is often confusingly used to cover all bio-based plastics (biodegradable and non-degradable) as well as the fossil-based biodegradable plastics. One could
reserve the label of “bioplastics” to “bio-based and bio-made plastics,” such as
polyhydroxyalkanoates (PHAs) or biopolymers such as silk, cellulose, or starch (see
Chapter 4). Such distinction should be limited to the scientific arena however, for
it adds little value for the larger public, beyond confusion on source and end-of-life.
An appendix in the tutorial (Chapter 4) further clarifies the spectrum of these
alternative plastics.

1.2 Plastics in the Environment – Biodegradation and
Impact of Litter

The biodegradation of polymers is a complex process that depends on many factors.
Some are determined by the polymer itself, but others are determined by the envi-
ronment such as T, pH, air, light, and density in microorganisms [1]. The suitability
of conditions ranges from industrial composting as most favorable environment to
home composting, soil and sludges, to fresh water and, finally, sea water and landfill
as least favorable ones.

Rao and coworkers (Chapter 2, [5]) elegantly showed that biodegradation pro-
ceeds in three major steps: (i) formation of a biofilm – a colony of various wild
microorganisms – on the plastic, (ii) depolymerization to low-$M_w$ components after
excretion of various enzymes onto the plastic, and (iii) ingestion and conversion
of the low-$M_w$ components as “feed” for the microorganisms. The polyolefins and
aromatics polymers that form most today’s polymers are generally recalcitrant
to the first two steps of biodegradation: their high hydrophobicity makes them
inhospitable for microorganism to form biofilms and their continuous C–C chains
are difficult the break by excreted enzymes. In contrast, condensation polymers
such as polyesters, polysaccharides, and polyamides are generally more prone to
biodegradation as their hydrophilicity allows biofilm formation and their weaker
C–O or C–N bridges in the main chain are prone to enzymatic hydrolysis and
cleavage. In this latter case, the rate of biodegradation can further be tuned by
numerous parameters. For instance, one can tune the accessibility of the main chain
e.g. by tuning its crystallinity. But one can also tune the hydrolytic reactivity of the
weak links by selecting a reactive hemiketal bond (in polysaccharides), a reactive
aliphatic ester bond (in aliphatic polyesters), or a more recalcitrant aromatic ester
(in polyethylene terephthalate [PET]), or amide one. The intrinsic recalcitrance
of polyolefins can also be tamed by pretreatment or adding oxidation or photoox-
idation catalysts. Such tunability will come handy to adjust the biodegradability
of plastic to their use and end-of-life. Interestingly, for some biopolymers such as
the natural polyamide silk, the degradation pathways and microorganisms have
not yet been elucidated. This is perhaps a good proof that research into biodegra-
dation mechanisms for plastics is still developing and that many open questions
remain.

Tian et al. (Chapter 3, [4]) quantitatively describe the magnitude of the prob-
lem of plastic litter and its environmental impact, which is striking, both with very
visible and truly hidden components. They also provide estimates on the extremely
long lifetime of plastic items, with over 200 years for a plastic straw. Their chapter focuses on the scale of the issue and the different sources of macroplastics as well as micro- and nanoplastics. Microplastics are generated through various routes, e.g. mismanagement of waste, accidental release, microplastics additives to products, the degradation of outdoor objects or natural wear of products, e.g. from rolling tires and washing textiles. While the ecological impact is visible, e.g. in birds strangled in waste plastics, the economic and human health impact, especially of microplastics, is less well documented. In the context of this chapter, the importance of biodegradability is introduced: even though some degradable plastics are not biodegradable according to home or industrial composting standards, they still degrade at significant rate to be considered as “non-persistent” chemicals. Polylactide (PLA), for instance, would fail home composting in under a year, but it is expected to degrade within a few years in ambient conditions, while PET would require 100+ years. Time will tell what rates of degradation would lead to a manageable steady state vis-a-vis leakage and littering. Finally, Tian et al. present a list of solutions and mitigations to the plastic conundrum with, among others, a focus on material design and on waste management.

Building on these two chapters, it is important to stress that biodegradability should be discussed in a more nuanced way than the binary “biodegradable and non-biodegradable” that is presently applied. Today’s strict biodegradation label is meant to make industrial biodigesters affordable by ensuring a limited reactor size and residence time for a given load of generally known plastics. But this definition should really be limited to compostable materials, while the broader label “biodegradable” should be used to also cover materials that slowly degrade in nature [17] and can, thereby, qualify as non-persistent pollutants, which is arguably the truly critical property to consider for protecting our environment. The difficulty is to assess (and certify) the level of non-persistence in natural conditions or thus to establish what an acceptable rate of biodegradation would be.

1.3 Biodegradable Polymers

The scene being set, we will now dive deeper into the world of polymers, with their raw materials, synthesis, structure, performance, and end-of-life options. We will start with the fossil-based polymers that are dominating the market today and then, present some bio-based alternative materials, some old ones and some very novel. Today’s polymers are mostly derived from fossil hydrocarbons, mainly crude oil, as discussed by Gruter and Lange (Chapter 4, [6]). The largest fraction is made of vinlyc monomers $H_2C=C(R)-X$ that can be polymerized in a variety of vinyl polymers with continuous carbon chains such as polyolefins, polystyrene, polyvinylchloride (PVC), or polyacrylate. But a smaller fraction of polymers contains heteroatoms in their main carbon chain, which come from polymerizing monomers through ester bonds (—C(O)O—), amide bonds (—C(O)—NH—), acetal bonds (—C(OR)2—), urethane or carbamate bonds (—C(NH)—O—), or carbonate bonds (—O—C(O)—O—). These can simplistically be referred to as condensation
polymers, whereas the former ones are referred to as addition polymers. The majority of the polymers consist of thermoplastics that are shaped and reshaped at will by melting, shaping (e.g. to desired bottle, film, or fiber), and finally cooling for use. Occasionally, some of these polymer chains can be bound or cross-linked to one another to form rigid thermosets for specific application such as tires, mattresses, or coating. While most polymers are still derived from fossil feedstock today, a small, though growing fraction is made of renewable feedstock such as sugars or vegetable oils.

Polymers have become very popular today because they combine several valuable properties (Chapter 4): lightweight, tunable strength and elasticity, easy shaping and coloring, tunable transparency, thermal/electric insulation, and many more. These properties are rewardingly exploited for a variety of applications. Some include rigid containers and castings, flexible films for packaging, rigid sheets for finished two-dimensional articles, fibers for textiles and ropes, foams for cushions and mattresses or all kinds of surface coverings, shock-absorbing joints or assembling agents such as coatings, adhesives, sealants, and elastomers. These various applications require totally different combinations of properties. Particularly demanding applications can further be reached by reinforcing polymers with strong materials such as glass or carbon fibers and, thereby forming composites.

The chemical composition of these polymers has a significant impact on the options that are available to responsibly manage plastic waste. For instance, most vinyl polymers are persistent pollutants when released into the environment. When collected, however, they are generally good candidates for chemical recycling to hydrocarbon feedstock, eventually via cracking or other stringent chemical modifications. Condensation polymers are more readily susceptible to chemical depolymerization: their constituting monomers can directly be recuperated after solvolysis with for instance alcohols or even water. Moreover, these polymers are often also more prone to biodegradation, depending on the type of heteroatom linkages and of the concerned monomers. For instance, PET with aromatic flanked ester bonds degrades several orders of magnitude slower in natural conditions (and could be called persistent) than linear aliphatic polyesters such as polybutylenesuccinate (PBS). Condensation polymers are essential in all biodegradable plastic developments. They thus receive more attention in this book.

1.3.1 Polyesters

Polyesters are very promising materials because they offer a wide variety of properties, from rigid to flexible films and from hydrophobic to hydrophilic materials [18–22]. Moreover, they are readily depolymerized to their monomers by solvolysis, such as hydrolysis or alcoholysis, which is valuable for chemical recycling. From a polymer chemistry point of view, condensation polymerization equates removing water from the monomer during its polymerization. PLA can for instance be made via condensation polymerization or via ring opening from the anhydrous lactide. Chapter 5 [7] deals with true condensation polyesters.
or biodegradation. These depolymerization technologies are technically well developed but not yet deployed at scale by lack of economic rivers.

Stouten and Bernaerts (Chapter 5, [7]) present the synthesis and properties of a variety of aliphatic polylactides that can be made via dehydration (condensation polymerization). Some are based on aliphatic diols and diacids (e.g., 1,4-butanediol and succinic acid) or on aliphatic hydroxyacids (e.g., lactic acid), while others may consist of aromatic monomers such as terephthalic acid. Their properties can be derived from the expanding set of known polyesters tested by many academic and industrial groups. For instance, aliphatic polylactides built on short-chain monomers tend to be rather stiff, whereas those built on long-chain monomers are more flexible and show a lower $T_g$. But polylactides can also be made stronger and stiffer by using more rigid monomers such as terephthalic acid and its emerging incumbent furanic dicarboxylic acid (FDCA) but also cyclic aliphatic diols such as isosorbides. Aliphatic polylactides are notoriously easier to depolymerize by hydrolysis or alcoholysis than their aromatic counterparts. Hence, they are also widely used in fast(er) degrading single-use applications e.g. in medical articles, in agriculture (e.g. for covering fields) and, increasingly, in packaging or single-use goods (Chapter 5, [7]).

Koller and Mukherjee (Chapter 6, [8]) dive further into a specific type of aliphatic polylactides, the polyhydroxyalkanoates (PHA), and discuss their unique manufacture and tunability. In contrast to most polymers discussed so far, PHA are synthesized in vivo by various microorganisms and stored as energy-rich granules to be metabolized when the microorganism falls short of carbon source; PHA are stored in microorganisms much like starch is stored in cereal and tubers for later plant/seed growth. This means that the PHA are designed to be biodegradable. These microorganisms can produce PHA from a variety of feedstocks, e.g., sugars, glycerol, or fatty acids but also synthesis gas (CO + H$_2$) or CO$_2$. They can also produce a large variety of PHA. The most common is based on 3-hydroxybutyric acid. But over 150 monomers have been identified. This versatility allows the microorganisms to produce PHAs with a large variety of properties. Koller et al. discuss the conditions required to produce various PHA and the challenges encountered to recover the PHA from the organisms. The PHA is often recovered from the microorganism by solvent extraction, occasionally assisted with cell disruption. This has for long remained a critical step in the production cost and has, therefore, hampered the deployment of PHA. Recent advances in the field help in reducing the production cost to promote their long-awaited growth in the market.

Narmon et al. (Chapter 7, [9]) deliver a detailed tutorial on ring-opening polymerization (ROP) as a sustainable and scalable strategy for high-molecular-weight polymers. The chapter dives into (mostly aliphatic) polyesters made from lactones. The most famous and commercially available polyesters from ROP are PLA and PCL. A primer to the kinetics and thermodynamics of ROP is given, where ring strains are key, as well as routes to functionalized ROP-based polyesters. Functionalization can be a valuable strategy to lower crystallinity and increase hydrophilicity, which are crucial in determining the polymer’s biodegradation potential. Functionalization can be introduced either through ROP of substituted lactone monomers or through modification and grafting of the polymer. ROP-based
polyesters can be categorized based on the ring sizes (mostly 5–12 membered) of their lactone and dilactone monomers, which largely determine polymer properties and sometimes also their relation to degradability. An interesting example is the four-membered ring β-butyrolactone, which offers an alternative route (via ROP) to the most popular PHA, poly(3-hydroxybutyrate). Although a lot of functional and structurally different lactones (and their polyesters) have been reported, only few clear structure–degradation relations have been developed thoroughly, most notably for co-polymers of lactide (PLA-based co-polymers). Assessment methods for hydrolytic degradability are not uniform and thus briefly but critically discussed.

1.3.2 Polysaccharides

Bio-based and biodegradable polymers are not limited to polyesters, however. The most traditional and abundant biodegradable polymers are not polyesters but polysaccharides [23]. Regenerated celluloses are traditional material for textile fibers (rayon) or films (cellophane), while thermoplastic (i.e. plasticized) starches are used in packaging and plastic bags. The originally stiff polysaccharide materials are softened by capping the free hydroxyl groups, e.g. in ester (–O–(O)C–) or xanthate groups (–O–(S)C–S–) or by inserting low-$M_w$ plasticizers such as glycerol [24, 25]. But a variety of novel polysaccharide materials are also being developed, e.g. based on microbial polysaccharides.

In Chapter 8, [10] Molenveld and Slaghek discuss the class of cellulose-based plastics in detail. Being among the first thermoplastic polymers, they have found their way to applications based on decent mechanical and optical properties. Key to rendering the non-plastic cellulose into a thermoplastic is chemical modification, e.g. by esterification of 1–3 of the three OH groups available (per mole of glucose entity) to tune the solubility and thermal properties and therefore its application. The chapter reports new developments on the esterification process, e.g. using new solvents or mixed esters, as well as on plasticizing and blending studies. Critically, the cost and sustainability of the cellulose plastics is to a large extent determined by the post-processing or derivatization steps. Finally, even though these plastics have been around since the nineteenth century, there is still little fundamental insight into the biodegradation mechanisms of the ester derivatives.

In Chapter 9, [11] Iwata and coworkers review the development of novel materials based on starch alternatives that are naturally produced by microorganisms instead of plants. These more exotic microbial polysaccharides connect glucose in different ways than do plants in cellulose and starch, namely through 1,3-, 1,4- or 1,6-glucosidic bonds in equatorial (α) or axial (β) configuration. Inspired by the development of modified cellulose and starches discussed in Chapter 8 and elsewhere [8, 9], the free hydroxyls of these microbial polysaccharides can be capped by various groups, e.g. by various ester groups, to tune the final properties of the material. This allows the production of adhesives, polyolefin-like plastics, or high-performance engineering plastics, occasionally with unique optical transparency. Such modifications are also affecting the biodegradability of the polysaccharides by affecting their affinity for biofilm formation and affecting the
accessibility of the hydrolysable hemiketal/glycosidic bond. Lee et al. thus briefly review the microbial synthesis and modification (esterification). As in the case of PHA discussed above, the extraction of the polysaccharide is likely to be a critical part in the industrial production of such materials.

### 1.3.3 Lignin

If polysaccharides are the most abundant biopolymers on earth, lignin is the second most abundant one. It is therefore not surprising to see much research devoted to upgrading lignin to materials [26–28]. Thermosets have historically been prime targets. Their synthesis generally consists of fixing functional groups to the lignin to allow cross-linking, or by using lignin as partial replacement of phenol in phenol–formaldehyde wood glue. But much more can be done with lignin, as discussed by Sarkanen and Chen in Chapter 10 [12].

Sarkanen and Chen (Chapter 10, [12]) first shatter the myth that process lignin such as kraft lignin would be highly cross-linked material. Instead, lignin is a linear phenolic polymer of ~2 kDa that reversibly associates to form complexes of ~20 kDa in alkaline water and of 2000 kDa in polar organic solvents after derivatization. This tendency to associate can be exploited to produce materials with tensile strength comparable to polystyrene (PS) by derivatizing various lignins and by adding minor amounts of monomeric or polymeric components. Interestingly, the lignin is biodegradable by organisms with strong oxidation capabilities and radical-generating enzymes such as laccases found in white-rot fungi. This opens the path toward fully biodegradable lignin-rich thermoplastics, when blended with biodegradable additives. Apart from that, the randomly substituted aromatic moieties in lignin have attracted the attention of chemical experts that want to link them to BTX (benzene–toluene–xylene) – the classical precursors for many high-performance materials, including many polyesters and polyamides – or to renewable bisphenol alternatives – monomer to polyesters, epoxy-resins, and polycarbonates [29].

### 1.3.4 Vitrimers – Recyclable Thermosets

So far, the discussion has been focused on thermoplastic materials and on the options that we have to make them bio-based and biodegradable. But one also needs to pay attention to the smaller, though important family of thermoset resins that are valuable (or required) in specific applications, e.g. for durable rigid structures, for elastomers, or for foams. These materials generally present challenges for responsible end-of-life management because they are difficult to recycle and equally difficult to biodegrade, as discussed in Chapter 11 [13].

An emerging family of polymers is attempting to mitigate these challenges, namely the covalent adaptive networks (CANs) and, particularly, the vitrimers (associative CAN). As demonstrated by Pitet and coworkers (Chapter 11, [13]), these materials consist of polymers that are cross-linked by reversible covalent bonds and are designed such that the cross-link can open and close reversibly and flexibly upon
heating. Hence, these materials combine the typical creep resistance of thermosets at application temperature with thermoplasticity at elevated temperature that allow mechanical recycling by remolding/reshaping. Pitet et al. nicely present the various types of adaptable cross-links that have been developed so far, discuss the resulting thermal behavior and the impact on self-healing and recyclability.

Vitrimers are intrinsically condensation polymers, with heteroatoms in the main chain and with cross-linkers to build the network. This offers the potential (though not the promise) to also recycle them chemically by depolymerization to the monomer. Similarly, this makes them candidates for non-persistent materials and, possibly, even biodegradable materials. The complex chemistry required to produce the monomers may however limit their use to high-value niche applications.

1.4 Beyond Biodegradation

1.4.1 Recycling and End-of-Life

Coming back to the root causes of the accumulation of plastic litter in the environment, this book has now discussed the second root cause: the persistence of today’s plastics and the potential to design novel non-persistent plastics. However, it has left the solution of the first root cause, the human behavior and lack of infrastructure, to the social and political sciences. Strong governmental leadership can minimize the first root cause by sensibilizing the consumer and providing efficient collection infrastructure for plastic waste, as found in numerous high-income countries. Once that is reached, the challenge comes back to the technology: what do we do with this collected plastic?

The industry has been struggling to (mechanically) recycle collected waste plastic in an economically viable manner for a few decades already. But this seems to be changing, now that consumers and society at large are pushing for solving this problem (Lange, Chapter 12, [14]). Much progress has already been achieved in mechanical recycling of the highest quality materials. The industry is now developing or resuscitating complementary technologies that can recycle spent polymers of lesser quality, i.e. by depolymerizing condensation polymers back to their monomers and by cracking addition polymers back to their general hydrocarbon feedstock. The residual waste fractions of the poorest quality can still be valorized by gasification, pyrolysis, or liquefaction technologies to produce chemical feedstock or liquid hydrocarbon fuels. But the residual waste, which is often called RDF or residue-derived fuel, can also be incinerated for energy recovery. Incineration can proceed either directly or indirectly after digestion of the organic fraction to biogas. Biodegradation eventually comes at the bottom of this valorization cascade, as it destroys the waste without producing any valuable product, save for some low-value compost. But biodegradation becomes invaluable for the fraction of materials that eventually ends up in the environment. Also, material recycling can’t proceed eternally, for it suffers from material losses at all stage. Full closure of the carbon cycle requires to compensate such carbon losses by virgin intake of atmospheric CO₂ via
natural or artificial photosynthesis (Lange, Chapter 12). Hence, bio-based plastics and, preferably, non-persistent ones are a necessary complement to recycling and an essential element of a circular chemical economy.

1.4.2 LCA

In view of all facets of plastics discussed above, there is a growing need to understand what makes (sustainable) sense and what not. Will proper end-of-life management allow the plastic economy to become environment friendly? Should society switch to novel and “greener” plastics, e.g., derived from biomass? Or should it return to more traditional materials such as wood/paper, metal, and glass/ceramic? These are very challenging questions to answer, for they require analysis of the whole life cycle of each option and consideration of many factors to properly assess the impact on land, water, air, and life and even external effects such as land-use change.

Li has devoted Chapter 13 [15] to highlight some of the challenges of such life-cycle analysis (LCA) and illustrating them by a study that tried to assess the environmental impact of replacing conventional plastics by bio-based ones in well-selected applications. Li reports important benefits for such substitutions. But she also shows that the benefits reached in some environmental aspects are often accompanied by penalties in others. This trade-off varies highly between cases and could change in the future by improving practices. This makes it difficult to draw general conclusions.

But LCA can also be applied to assess the environmental impact of recycling. Lange in Chapter 12 mentions a few studies that seem to converge in prioritizing mechanical recycling, over chemical recycling, over energy recovery and, finally, biodegradation.

1.4.3 Implementing the “New Plastics Economy”

This book has tried to address a few important technical aspects of the “New Plastics Economy.” But there is clearly more than technology in the overall toolbox to achieve this New Economy. Beyond why we need it, and which technical solutions are at hand to create it, there is one pervasive question that needs attention: “How will we navigate there?” While announcements for new plastics have been manifold over the last decades, their successes have been rare. The hurdles to overcome have been numerous: too long time to market, too much focus (no pivot possible), too little focus (no stable path found), too costly in capital expenditure (CAPEX) or operational expenditure (OPEX), and many more “too’s.” For mitigating all these excesses, some business experiences and guidelines are discussed by Nevejans and De Wildeman (Chapter 14, [16]). For instance, they warn for trying to copy the mature industry and discuss the Technology Readiness levels (TRLs) in the context of these new plastics. The chapter concludes with five useful innovation rules to keep in mind when companies or individuals want to participate in the production chain of the alternative plastics economy, three of which are worth mentioning here: start with small-volume high-value and applications (#1), take to time to develop it right (#2), and develop truly “green” product (#5).
1.5 Conclusions and Outlook

Overall, plastic biodegradability or, more accurately, non-persistence must become a design parameter in plastic products. But the discussion is generally oversimplified and mixed or confused with other properties such as bio- versus fossil-based. This has resulted in the general perception that bio-based plastics are biodegradable, while fossil-based ones are not. Additional confusion has been born from mixing strict composting requirements with the broader biodegradation requirements that make littered material non-persistent in nature. Environmental non-persistence should indeed be considered over a wide timescale, from weeks to decennia (maybe more), depending on the application of the polymer, on its expected end-of-life, and on the risk of it ending up in the environment as unintentional litter or as microplastics generated during normal use (e.g. tires and textiles). On one end of the scale, fast biodegradation is very valuable in medical applications such as sewing wires. It would also be valuable for single-use products that get contaminated heavily with food, e.g. throw-away cutlery and beakers or packaging of wet food and that could be composted along with the food waste. On the other end of the scale, durable products, e.g. those used in construction, particularly outdoor, should resist biodegradation for decennia. Many other applications fall between these extremes (medical degradation vs. durable multi-decade long functionality). It is therefore tempting to design biodegradation as the last step of the waste management hierarchy, after “reduce, reuse, and recycle.” Biodegradation should indeed neither hinder normal use and longevity of the product nor hinder its efficient recycling after use.

The chapters of this book have discussed opportunities in non-persistent materials. For instance, aliphatic polyesters such as PHA and PBS generally degrade rapidly in natural environments, whereas aromatic polyesters such as PET survive for much longer times, and PLA would be somewhere in between. Similarly, the modification of polysaccharides based, e.g. on starch or cellulose, allows to tune the rate of degradation besides tuning the mechanical properties. Sometimes, aligning the thermal and mechanical properties of such plastics with the application in mind can be a challenge. Even, lignin-based materials promise to be non-persistent through oxidative biodegradation by fungi. But other polymeric materials should also be considered, e.g. polyamides, polyethers, and polycarbonates. They all contain heteroatoms in their main polymer chain that offer anchor points to biofilms and biological attack. Selecting or chemically tailoring a condensation polymer (bio-based or not) for an application with substantial leakage to the environment – thus where the persistence has to be on the order of less than a few years – is in practice not an easy task. The degradation rate has to be somewhat in line with the leakage rate and what is deemed an acceptable accumulation in the environment. Multidisciplinary collaboration from the early stage of the research to high TRL levels may be necessary here, as the input of chemists (feedstock conversion and polymer design), engineers (processing, thermomechanical product properties), and biologists (biodegradation, toxicity, persistence) is needed almost simultaneously.

Interestingly, numerous non-persistent polymers are well suited for manufacturing from renewable carbon, being atmospheric CO₂ or biomass, e.g. sugars.
They are indeed rich in oxygen and/or nitrogen and contain, thereby, partially oxidized carbons, like these renewable resources. If today’s polymers are dominated by oxygen-free polyolefins, it’s largely due to the fact that these materials were well suited for production from the fossil oxygen-free hydrocarbon feedstock that the industry has been relying on throughout the twentieth century up to today. This represents an additional opportunity for deploying a new, sustainable, and circular plastic economy.

Looking beyond biodegradable plastics, a new circular plastic economy needs to start by recycling the spent plastic back to new materials [1]. Combining mechanical and chemicals recycling is not expected to fully close the carbon cycle, however. Carbon will inevitably be lost at all stages of the material cycle. These losses need to be compensated for by input of fresh carbon, preferably, fresh renewable carbon. Non-persistent bio-based plastic are well positioned to fulfill this task and simultaneously address the problems of carbon sourcing and carbon disposal in a circular and sustainable way [1, 2].

The transition from fossil to recycled and renewable carbon will take time, likely a few decades, as observed during the emergence of the petrochemical industry some 50 years ago. Technologies are indeed expected to start at modest scale and modest efficiency and, consequently, at high cost. The new polymers will likely grow slowly by proving themselves in high-value and small-volume applications at first instance. As technologies and feedstock supply mature and develop in scale, the production costs will decrease, which opens access to larger and more diverse markets, eventually, up to commodity applications. A simple, though ambitious deployment model suggests indeed that the use of fossil carbon may peak at twice today’s level by 2040 (Figure 1.2), to be overtaken by recycled and renewable carbon after 2050 and drop to 10% of the chemical diet only by 2070 [2].

To proceed smoothly and cost effectively, this transition must be supported by numerous measures, many of non-technical nature. Starting with the non-technical ones, society must stimulate and reward producers, distributors, and consumers to switch to sustainable products, even if these are less convenient or (initially) more expensive. Stimulation may start with ethics, by promoting the harmony between humans themselves and with their environment. But more will be needed. Society must adjust the regulation and certification to help consumers recognize truly circular and sustainable products and nudge them to choose these products. Regulators must also support sustainable solutions financially, e.g. by taxing resource utilization and waste production at higher rate while taxing labor at lower one. They must also harmonize their support for sustainably energy and materials to allow both sectors to compete fairly for the same feedstock. This is presently not the case in many regions that heavily support subsidize or mandate low-carbon energy but not low-carbon chemicals.

But society must also stimulate technology innovation, while watching out for undesired technology lock-in. Society must stimulate the sorting and recycling of today’s fossil plastics while preparing the recycling of tomorrow’s renewable plastics. The same warning applies to the “design for recycling” that will naturally attempt to restrict the number of materials but should nevertheless stimulate the emergence of
tomorrow’s renewable and non-persistent plastics. Finally, regulators and financial instances must support pioneers to try out sometimes far-stretched ideas, for some could form a cornerstone of the New Plastics Economy one day.

The definition and development of a new circular plastic economy presents enormous challenges. But it also offers unique opportunities for young scientists to contribute to the design of their future. For all of us, a mantra (or a cascade of measures) that frames the role for biodegradable plastics in the overall rethink of the plastics economy, but equally holds for other material economies, is found in Box 1.1.
Box 1.1 4R mantra for rethinking material economies, managing natural resources, and safeguarding the environment

- **Reduce** the consumption of goods.
- **Reuse** spent goods in all possible ways.
- **Recycle** the materials into new goods.
- **Regenerate** the environment with the carbon that we can’t use or that escaped our control (biodegradation in case of leaked plastics)

**Note in proof:** While finalizing this book we recognized some shortcoming in our scope. For instance, we could have presented a better coverage of the physical and mechanical properties of the emerging plastics and of the challenges these, as well as in situ degradation, may present in the processing to final goods. We also failed to recognize the emergence of design for “triggered” (bio)degradation that aims at controlling the onset of biodegradation (mostly after use) by triggers like radiation, heat, humidity, or chemical stimuli. This could be of use in niche applications, but it might conflict with a design for recycle. The reader is invited to explore these fields to complete the picture developed in this book.

**References**


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